

Water transport through functionalized nanotubes with tunable hydrophobicity

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Molecular dynamics simulations are used to study the occupancy and flow of water through nanotubes comprised of hydrophobic and hydrophilic atoms, which are arranged on a honeycomb lattice to mimic functionalized carbon nanotubes (CNTs). We consider single-file motion of TIP3P water through narrow channels of (6,6) CNTs with varying fractions (f) of hydrophilic atoms. Various arrangements of hydrophilic atoms are used to create heterogeneous nanotubes with separate hydrophobic/hydrophilic domains along the tube as well as random mixtures of the two types of atoms. The water occupancy inside the nanotube channel is found to vary non-linearly as a function of f , and a small fraction of hydrophilic atoms ($f \approx 0.4$) are sufficient to induce spontaneous and continuous filling of the nanotube. Interestingly, the average number of water molecules inside the channel and water flux through the nanotube are less sensitive to the specific arrangement of hydrophilic atoms than to the fraction, f . Two different regimes are observed for the water flux dependence on f – an approximately linear increase in flux as a function of f for $f < 0.4$, and almost no change in flux for higher f values, similar to the change in water occupancy. We are able to define an effective interaction strength between nanotube atoms and water's oxygen, based on a linear combination of interaction strengths between hydrophobic and hydrophilic nanotube atoms and water, that can quantitatively capture the observed behavior.

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I. INTRODUCTION

Fluid flow through nanoscopic pores of carbon nanotubes has received significant scientific attention owing to the potential applications that may result from the use of nanotubes in various technologies^{1–4}. Examples include nanotube-based membranes for water desalination and purification^{5,6}, nanoscale transport for lab-on-a-chip devices⁷ and integrated circuits⁸. At the fundamental level, fluid flow through nanotubes is endowed with various interesting phenomena – breakdown of continuum hydrodynamics^{9,10}, temperature induced hydrophobic-hydrophilic transitions¹¹, novel phase behavior¹², etc. Moreover, nanotubes can be used as surrogates to study other complex flow systems such as biological channels like aquaporins¹³. Therein, carbon nanotubes can be used as a simple prototype devoid of complexity present in the biological channels, but nonetheless capturing some important physical details¹⁴.

Early molecular dynamics simulations by Hummer *et al.* showed that water can spontaneously fill the cavity of a (6,6) carbon nanotube and stay filled during the entire simulation time of 66 ns¹⁵. They observed a pulse-like intermittent transmission of water molecules through the nanotube with similar rates as biological channels. The transition between empty and filled nanotubes, realized by tuning interactions between nanotube atoms and water¹⁶, can be described as a two-state process¹⁷. Several

theoretical models have been developed that can describe water permeation through the nanotube channel at equilibrium¹⁸ as well as in the presence of a driving force such as pressure or chemical potential difference¹⁹.

While simulations on pristine CNTs have provided invaluable fundamental insight into water flow therein, functionalization of carbon nanotubes²⁰ is often either a prerequisite for their processing, e.g., the use of surfactant for solution dispersion²¹, or desirable to achieve certain functionality such as sensitivity and selectivity in molecular detection²². Moreover, nanotubes with similar structural features as CNTs, but different atomic composition such as Boron-Nitride²³, carbon doped Boron-Nitride²⁴, and various inorganic materials²⁵, can now be synthesized routinely in the laboratory. In the context of CNT-surrogate study of flow through biological channels, nanotube-water interactions can vary depending on the hydrophobicity of the amino acids involved. In all of these cases, as the interactions between nanotube atoms and water will change depending on the nanotube functionalization and composition, the water filling and permeation behavior will also be different. While the understanding of water flow through functionalized nanotubes so far is quite limited, simple models that incorporate basic details of nanotube functionalization may enable important progress in understanding fluid flow through nanotubes of a broader range of composition and function.

In this paper, we use molecular dynamics simulations to study water flow through model tubular channels in which atoms are arranged on a honeycomb lattice, and two different atom types are used to populate the lattice

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sites, resulting in a binary heterogeneous nanotube. The two types of nanotube atoms differ only in their Lennard-Jones parameters with respect to water, and correspond to sp^2 -hybridized carbon C (labeled hydrophilic due to continued filling of the nanotube with water) and reduced carbon-water interaction strength C' (termed hydrophobic as the nanotube is mostly empty but undergoes transition between empty and filled states) as used by Hummer *et al.*¹⁵. We note that our classification of nonpolar sp^2 -hybridized atoms as hydrophilic is different from previous work where the nanotube made up of such atoms was actually characterized as hydrophobic¹⁵. We have based our classification on the water droplet contact angle on a flat unrolled nanotube surface; for C atoms the contact angle is less than 90° (hydrophilic) and for C' atoms the contact angle is slightly above 90° (hydrophobic)¹⁶. We first vary the fraction, f , of hydrophilic nanotube atoms, separated axially from the hydrophobic nanotube atoms, to study its impact on water filling as well as water flow through the nanotube. In addition, for a given f , we also study the influence of nanoscale patterning on water flow by arranging hydrophilic nanotube atoms in various patterns. Finally, we propose a simple mean-field model, in which the heterogeneous nanotube is represented as a homogeneous nanotube with uniform interactions between the nanotube atoms and water. We show that the predictions of this simple model are in very good agreement with the detailed simulation data.

II. MODEL AND SIMULATION DETAILS

To study the flow of water through functionalized nanotubes, a single (6,6) nanotube, with diameter of 0.81 nm and length 1.34 nm, is solvated in a periodic TIP3P water box with 1025 molecules. The nanotube is free to translate and rotate throughout the simulation time. The simulations are performed in an NPT ensemble using molecular simulation package GROMACS (version 4.0.7) for 100 ns with a timestep of 2 fs. The temperature is maintained at 300 K using the Nose-Hoover thermostat, and the pressure is maintained at 1 bar using the Parrinello-Rahman barostat with a time constant of 5 ps. We use the particle mesh Ewald (PME) method²⁶ for long-range electrostatic interactions with a short-range cutoff value of 0.9 nm. For short-range Lennard-Jones (LJ) interactions, we use a cutoff value of 1.4 nm. The well-depths of the Lennard-Jones potential between the nanotube atoms and water's oxygen atom are 0.4784 kJ/mol (hydrophilic) and 0.2703 kJ/mol (hydrophobic), with the corresponding LJ diameters being 0.3275 nm (hydrophilic) and 0.3414 nm (hydrophobic). The angle and dihedral potentials are also applied to the nanotube atoms as done previously¹⁵.

III. RESULTS AND DISCUSSION

To understand the dependence of water flow through cylindrical channels with both hydrophobic and hydrophilic building blocks, we use carbon nanotube like short cylindrical channels made up of hydrophobic and hydrophilic atoms. The fraction of hydrophilic atoms (f) is varied to tune the relative proportions of these atoms in order to change the water occupancy and flow characteristics of the resulting nanotubes. Previously, Hummer *et al.* have shown that fully hydrophilic nanotubes ($f = 1$) of the same size stay filled with an average occupancy of about 5 water molecules, and conduct about 17 water molecules per nanosecond¹⁵. On the other hand, fully hydrophobic nanotubes ($f = 0$) can transition between filled and empty states with an apparent two-state kinetics¹⁷. Melillo *et al.* performed a systematic variation of interaction strength between nanotube atoms and water's oxygen to show that water occupancy and flow is sensitive to changes in the interaction strength within only a narrow range¹⁶. For low attraction strengths, the nanotubes stay empty with no flow, whereas for high attraction strengths, the nanotubes are filled and conduct water with similar rates. For intermediate attraction strengths, a sharp increase in water occupancy and flow was observed, which was related to the change in wetting characteristics based on simulations carried out on the unrolled nanotube surface.

Recent work from Debenedetti and co-workers has highlighted the importance of surface heterogeneity and patterning on nanoscale hydrophobicity as it relates to the behavior of confined water^{27,28}. Some of the complexities associated with water flow through heterogeneous channels have been addressed using charged nanotube atoms¹⁴, asymmetrically positioned charges²⁹, and Y-shaped nanochannels³⁰. For nanotube surfaces comprised of hydrophilic and hydrophobic atoms, the sensitivity of water flow to the corresponding surface heterogeneity, the fraction of hydrophilic atoms, and the actual patterning of these atoms into hydrophobic and hydrophilic domains, is much less clear.

Figure 1 (left panel) shows the number of water molecules occupying the nanotube as a function of time for varying fractions of hydrophilic atoms, $f = 0, 0.25, 0.5, 0.75$, and 1 (from top to bottom). In this case, hydrophilic and hydrophobic atoms are distributed along the nanotube axis termed 'axial arrangement' to distinguish it from other arrangements considered in this work. As expected on the basis of earlier findings, the fully hydrophobic nanotube ($f = 0$) undergoes transitions between empty and filled states, whereas the fully hydrophilic nanotube ($f = 1$) stays filled during the entire simulation time. Interestingly, we find that just a small fraction of hydrophilic atoms ($f = 0.25$), localized at the nanotube tip, is sufficient to significantly increase the number of water molecules occupying the nanotube. For $f > 0.4$, the nanotube stays completely filled.

To further quantify water occupancy as a function of

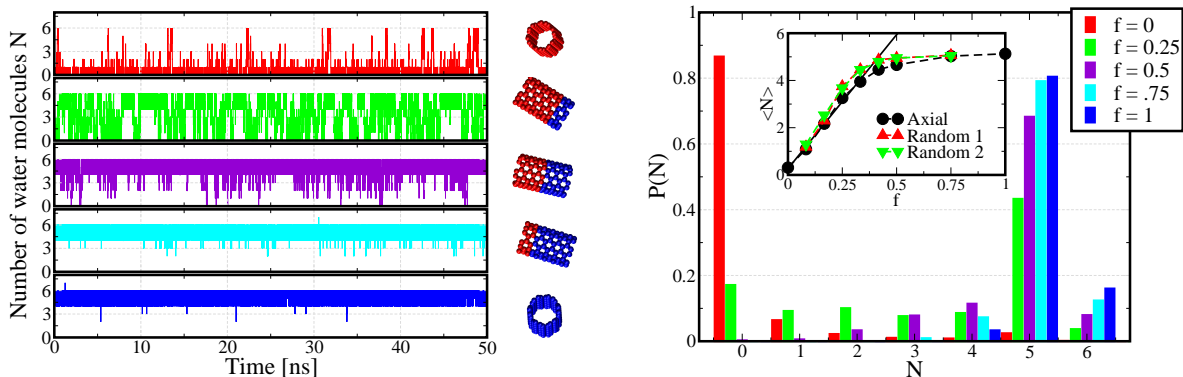


FIG. 1. Water occupancy. (Left panel) Number of water molecules N for varying fraction of hydrophilic nanotube atoms f are shown as a function of time. (Middle panel) Nanotube snapshots are shown, with hydrophobic and hydrophilic atoms labeled in red and blue, respectively. (Right panel) Probability of observing N water molecules inside the nanotube $P(N)$ is shown for various values of f . The inset shows average number of water molecules as a function of f for three possible arrangements of hydrophilic atoms.

f , we calculate the distribution $P(N)$, which is the probability of finding N water molecules inside the nanotube. The $P(N)$ for several representative values of f are shown in Fig. 1 (right panel). The probability of observing an empty nanotube, $P(0)$, decreases dramatically with increasing number of hydrophilic nanotube atoms (i.e., increasing f to 0.5). This precipitous decrease in $P(0)$ is complemented by a similarly dramatic rise in the probability of observing $N = 5$ or 6 water molecules, whereas relatively little change in $P(N)$ is observed with subsequent increase in f from $f = 0.75$ to $f = 1$. As shown in the inset of Fig. 1 (right panel), the average number of water molecules inside the nanotube $\langle N \rangle$ changes approximately linearly as a function of f for $f < 0.4$ and then plateaus at a value found for the fully hydrophilic case. The so-called ‘axial arrangement’ is the same as depicted in Fig. 1, which is obtained by separating continuous domains of hydrophilic and hydrophobic atoms along the nanotube axis. The so-called ‘random arrangement’ is obtained by placing the hydrophilic atoms randomly on the nanotube lattice (lattice sites numbered from 1 to 144), with two different cases considered here by changing the seed of the random number generator.

In addition to water occupancy, water transport and its potential sensitivity to tube properties, are important to quantify. To probe the effects of changing the fraction of hydrophilic atoms on water flux through the nanotube, we calculate the number of water molecules that permeate the nanotube by entering either end, but leaving from the opposite end over the total simulation time. Water flow is defined as the number of water molecules transmitted per nanosecond through the nanotube. Figure 2 shows water flow as a function of f for three possible arrangements of hydrophilic nanotube atoms. For reference, we show the value of water flow obtained by Hummer *et al.*¹⁵ for the fully hydrophilic nanotube ($f = 1$).

First, focusing on the data for the axial arrangement of hydrophilic and hydrophobic atoms in Fig. 2, we ob-

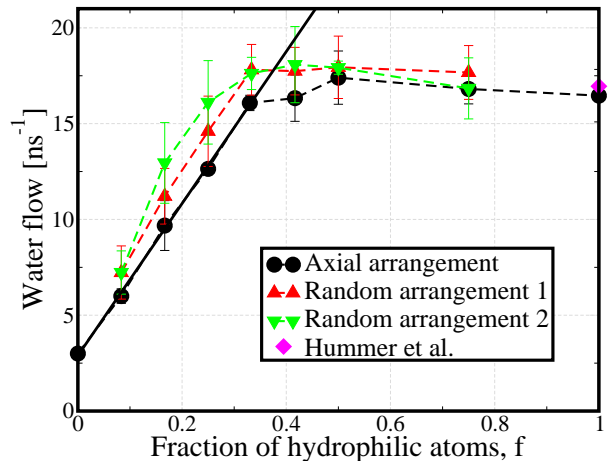


FIG. 2. Water flow rate. Number of water molecules permeating through the nanotube, which enter either side and leave from the opposite side, per unit time, are shown as a function of fraction of hydrophilic atoms f . The symbols connected by dashed lines are the simulation data and the solid black line is the linear fit for $f < 0.4$ for the ‘axial arrangement’ data.

serve an approximately linear dependence of water flow on f for $f < 0.4$. Outside this regime, the water flow is relatively insensitive to the increase in f , and a slight decrease in water flux is observed with increasing f . The linear dependence of water flow as a function of f for $f < 0.4$ likely appears due to the concomitant linear relationship between water flow and occupancy, shown for the same condition in Fig. 1 (inset). A similar change in water occupancy and flow was reported previously for a spatially uniform change in nanotube-water attraction strength over low to moderate interaction strengths¹⁶. There, an increase in the nanotube-water attraction strength was shown to monotonically increase water’s residence time inside the nanotube. For higher attraction strengths, this increase in the residence

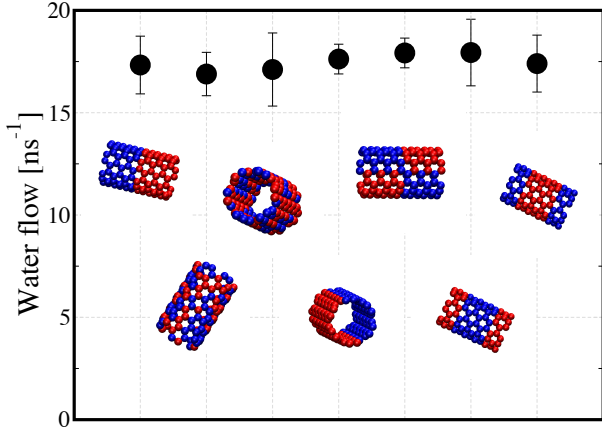


FIG. 3. Number of water molecules permeating through the nanotube, which enter either side and leave from the opposite side, per unit time are shown for various arrangements of hydrophilic (blue) and hydrophobic atoms (red) for $f = 0.5$ as depicted in the nanotube snapshots.

time led to a decrease in water flow, thereby deeming both the average water occupancy and the residence time important for capturing the change in water flow. In the case of heterogeneous nanotubes, an increase in the fraction of hydrophilic atoms above $f = 0.4$ leads to a slight increase in water occupancy (Fig. 1), but insensitive or subtly decreasing water flow (Fig. 2). Therefore, the water flow characteristics appear to be influenced similarly by a heterogeneous distribution of hydrophilic and hydrophobic atoms as compared to a spatially uniform change in nanotube-water interaction strength.

To see if the specific axial arrangement of hydrophilic atoms is responsible for the observed behavior, Fig. 2 also shows water flow as a function of f for random arrangements of hydrophilic atoms. The qualitative behavior is quite similar in all cases, with approximately linear dependence for low f values and a plateau (or slight decrease) for higher f values.

Though statistically less significant, a slight increase in water flow for a given fraction of hydrophilic atoms is observed in the case of the random arrangement as opposed to the axial arrangement. The water occupancy data (Fig. 1, right panel inset) also shows a similar trend, with the random arrangement leading to slightly higher water occupancy. One can explain this based on previous work by Giovambattista *et al.* where it was shown that hydrophilic borders surrounding nanoscale hydrophobic patches can significantly alter water hydration by reducing the water repulsion²⁷. In the ‘random arrangement’ case, the hydrophilic atoms are mixed with hydrophobic atoms, thereby enhancing water density near such surfaces, which can lead to slightly enhanced water flow.

Between the cases of axial and random arrangement of hydrophilic and hydrophobic atoms exists a range of cases wherein discrete domains could conceivably pattern the nanotube surface. To further probe how such specific

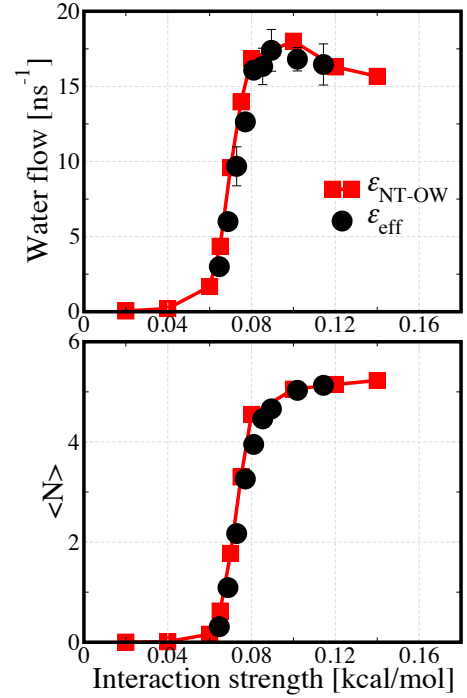


FIG. 4. Flow through homogeneous versus heterogeneous nanotubes. (Top panel) Number of water molecules permeating through the nanotube, which enter either side and leave from the opposite side, per unit time are shown as a function of interaction strength between nanotube atoms and water’s oxygen. For nanotubes comprised of hydrophobic and hydrophilic atoms, we use eq. 1 to estimate an effective interaction strength ϵ_{eff} , whereas separate simulations are conducted for nanotubes comprised of a single type of atoms interacting with water’s oxygen with $\epsilon_{\text{NT-OW}}$. (Bottom panel) Average number of water molecules as a function of interaction strength between nanotube atoms and water’s oxygen.

arrangement of hydrophilic atoms (e.g., on the ends of the nanotube) may modulate water flow, we simulate several possible arrangements as shown in Fig. 3, all for $f = 0.5$. Within statistical uncertainty of the measured water flow rate, the different heterogeneities studied produce similar results. As the water flow through these short nanotubes is expected to be dominated by the barriers at the entry and exit of the nanotube⁵, the observed insensitivity of water flow to the actual arrangement of hydrophilic atoms is a bit surprising. While this effect may be tuned by increasing nanotube length and for low values of f , this requires future work employing either a low-cost but accurate single-site water model³¹ or dipole lattice model of water³².

The qualitative similarity we observe here in water flow through heterogenous nanotubes made up of two types of atoms with previous work on homogeneous scaling of nanotube-water interaction strength, begs the question about whether these two cases may be related in a more quantitative way. Due to the observed insensitivity of the water occupancy and flow on the actual arrangement of

the hydrophilic atoms, we *hypothesize* that one can define an effective interaction strength ϵ_{eff} between nanotube atoms and water's oxygen as,

$$\epsilon_{\text{eff}} = \epsilon_{\text{philic}}f + \epsilon_{\text{phobic}}(1 - f), \quad (1)$$

where ϵ_{philic} and ϵ_{phobic} correspond to the LJ interaction parameters between nanotube atoms and water's oxygen for hydrophilic and hydrophobic atoms, respectively. Such a linear interpolation is also justified based on the small differences in the interaction potential curves (LJ potential) between the two cases¹⁵. To test if such a simple scaling relationship works over a broad range, we calculate water flow through a nanotube and average water occupancy for various nanotube-water interaction strengths $\epsilon_{\text{NT-OW}}$. The comparison of this data with water flow data from Fig. 2 and water occupancy data from Fig. 1 (right panel inset) is shown in Fig. 4. Overall, the change in water flow and $\langle N \rangle$ as a function of uniform change in nanotube-water interaction strength, as predicted by detailed simulations, is in remarkably good agreement with the prediction based on the mean-field type description in Eq. 1 for heterogeneous nanotubes. This quantitative agreement in Fig. 4 suggests that the fluid flow through functionalized nanotubes may be a simple function of a parameter describing the affinity between the fluid molecules and the nanotube surface. The apparent insensitivity to the distribution of the two atom types may be a manifestation of the single-file nature of water flow through a (6,6) nanotube. This highlights the question for future study regarding whether deviations from a mean-field description become significant for larger diameter nanotubes or not. In addition, it will be useful for future studies to elucidate any sensitivity of the observed behavior to nanotube length.

IV. CONCLUSIONS

We have studied the water filling and transport through a simple model of functionalized carbon nanotubes. The fraction of hydrophilic atoms, f , are varied to change the nanotube from fully hydrophobic ($f = 0$) to fully hydrophilic ($f = 1$). Two different regimes are identified for water occupancy and flow as a function of f . For low f values ($f < 0.4$), there is an approximately linear dependence on f of the average number of water molecules inside the nanotube as well as the number of water molecules transmitting through the nanotube. For higher f values, a slight increase in water occupancy is observed, whereas a slight decrease in water flow is predicted. For most of the systems considered in this work, the observed water flow properties are relatively insensitive to the precise arrangement of hydrophilic atoms. A simple mean-field type expression for effective interaction strength between nanotube atoms and water can be used to quantitatively capture flow characteristics of water through heterogeneous nanotubes. These findings

suggest that control over the character (i.e., interactions with water) of the nanotube functionality may be more important than the specific spatial arrangement of that function for controlling water flow therein. This simple design principle should enable prediction of flow characteristics in synthetic and functionalized nanotubes beyond pristine CNT and help guide rational design of target functionality.

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